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VIBRATIONAL SPECTRA AND THE DIBORANE STRUCTURE

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The problem of structure of diborane, the simplest of hydrides of boron, has been getting the attention of numerous investigators for a number of years. The diborane molecule is different from others in one important respect -- it has twelve valence electrons to satisfy more than six bonds. Several authors offered various models for the structure of diborane molecule. At first many authors ascribed to diborane an ethane-like molecule H_3BBH_3 (I). B. V. Nevrasov [1] offered an ethylene-like structure (II)

with the two elements (BH_3) connected to each other by hydrogen bonds along the edge of a tetrahedron. Other authors (2,3) also postulated ethylene structure for diborane in which the atoms of boron and four of the hydrogen atoms are situated in one plane, while the other two are placed on a line perpendicular to this plane and passing through the middle of the B-B bond at equal distances from this plane. (ethylene-like model of diborane with two equal hydrogen bonds II). The answer to the question as to which of the above discussed structures is the correct one must be answered by experimental data.

It has to be pointed out that the electronographic analysis of diborane did not permit to make a definite choice and thus establish a definite model, since the theoretical intensity curves, calculated for models I and II, equally well fit the experimental curve (2,3). Later Hedberg and Schomaker, after making another electronographic analysis of diborane, interpreted their data in favor of model II. Many investigators have studied the vibrational spectra of diborane, attempting to interpret their results in terms of either model I or model II. Other authors (5) have interpreted the vibrational spectra in favor of ethane-like model. However, the latter interpretation has run into considerable difficulty: in the combination spectrum of B_2H_6 there are two very intensive polarized lines ~~2504 and 2104 cm^{-1}~~, which should correspond to the fully symmetrical B-H vibrations in the ethane-like model (symmetry D_{3d} or D_{3h}), instead of a single vibration frequency. Besides, the analysis of rotational structure of diborane by means of the infrared absorption spectra has shown (6) that the diborane molecule must have an asymmetrical top structure, whereas the ethane-like structure has perforce a symmetrical top structure. Analysis of vibrational infrared absorption spectra and study of combined scattering shows that there is a center of symmetry in the molecule. This limits the number of possible models, leaving only the flat and the "warped" models of diborane with two hydrogen bridges (bonds).

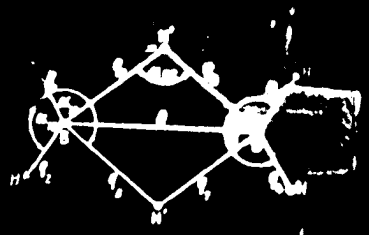
Analysis of a thin structure of one of the infrared absorption bands of diborane at 368 cm^{-1} (this band corresponds to a vertical vibration of the ring ) allows (6) to exclude the "flat" diborane model. In recent years the

majority of authors (6,7) have interpreted the vibrational spectra based on the modal II (symmetry V_h). The most comprehensive interpretation was offered in (7) on the basis of the comprehensive infrared absorption and combinational scattering analysis relating to type of lines, intensities, degree of polarization, etc., on molecules of $B_2^{10}H_6$, $B_2^{10}D_6$ and $B_2^{11}H_6$. In order to verify conclusively this interpretation (see Table 3) it is necessary, therefore, to have a theoretical calculation of normal vibrations of diborane on the basis of modal II. Such a theoretical calculation, on the basis of modal II, has been accomplished already (8).

It is not possible to recognize that calculation as satisfactory for the following reasons enumerated below. First the authors used a primitive valence-force modal as their basis, only considering the diagonal force coefficients in the potential energy matrix. Second, the authors allowed a gross error in counting for one of the vibrations (the nonplanar ring vibration) in the potential energy function expression, a factor proportional to the fourth power of displaced co-ordinates, instead of the second power. Third, the authors have erroneously interpreted the known at that time vibrational spectra of diborane.

Calculation of frequencies and force coefficients

Calculation of frequencies of normal vibrations and (steady state?) potential energies of diborane was carried out by the authors of this paper according to the method of M. A. Eliashevich (9).



Vibrational coordinates of diborane

In case of diborane there are 18 normal vibrations. For the purposes of calculation 29 vibrational coordinates were chosen -- describing changes in bond distances and bond angles (see above drawing):

$q_i (i=1-4)$, $q_i (j=5-8)$, q, α_{12}, α_{34}, β_i $(i=1-4)$, α_{ij} $(j=5-8)$, α_{56}, α_{78}, α_{ij} $(i=1, 2, j=5, 8;\ i=3, 4, j=6, 7)$

Considering the symmetry of diborane, the coordinates of symmetry are introduced. Vibrations of the following types of symmetry are:

$\Gamma = 4A_g + A_u + 2B_{1g} + 2B_{1u} + 2B_{2g} + 3B_{2u} + B_{3g} + 3B_{3u}$.

Introducing symmetr[illegible]al coordinates for the types of symmetry A_g, A_1 and B_{2g}:

[illegible]

$$q_5^{A_g} = \frac{1}{\sqrt{2}}(\alpha_{..} + \alpha_{..}), \; [illegible] + h_{.} + h_{.} + [illegible]$$

$$q_6^{A_g} = \frac{1}{2\sqrt{2}}(\alpha_{..} + \alpha_{..} + [illegible] \alpha_{..} + \alpha_{..} + \alpha_{..} + \alpha_{..});$$

$$q_7^{A_g} = \frac{1}{2\sqrt{2}}(\alpha_{..} - \alpha_{..} - \alpha_{..} - \alpha_{..} - \alpha_{..} + \alpha_{..} + \alpha_{..} + \alpha_{..});$$

$$q_5^{B_{2g}} = \frac{1}{2\sqrt{2}}(\alpha_{..} - \alpha_{.} [illegible] \alpha_{..} - \alpha_{..} - \alpha_{..} + \alpha_{..});$$

[illegible]e following eleven add[illegible]hips hold among the coordinates of symmetry:

$$[illegible]\,\mathrm{ctg}\,\frac{\theta}{2}\sqrt{2} - q_5^{A_g} = 0;$$

$$3)\; q^{A_g} a_1 \,\mathrm{cosec}\,\frac{\theta}{2} - q^{A_g}\,\mathrm{ctg}\,\frac{\theta_1}{2}\, a_1 + q_{.}^{A_g} = 0;$$

$$4)\; q^{A_g} a_1 \,\mathrm{ctg}\,\Phi \sin\frac{\theta}{2}\sqrt{2} - q^{A_g}\,\mathrm{ctg}\,\Phi a_1\sqrt{2} - q^{A_g}\,\mathrm{ctg}\,\Phi\,\mathrm{tg}\frac{\theta}{2} + [illegible]$$

$$5)\; q_5^{B_{1u}} - \frac{\cos\frac{\theta}{2}\sin\frac{\theta}{2}}{\sin\Phi}\sqrt{2}\,\beta^{B_{1u}} = 0;$$

$$6)\; q^{B_{1u}} a_1\,\mathrm{tg}\,\frac{\theta_1}{2} + a_{10}^{B_{1u}} = 0; \qquad (3)$$

$$[illegible]^{B_{..}} a_1\,\mathrm{ctg}\,\frac{\theta_1}{2} - a_{10}^{B_{..}} = 0;$$

$$[illegible]^{B_{..}} a_1\,\mathrm{ctg}\,\frac{\theta}{2}\sqrt{2} + a_5^{B_{..}} = 0;$$

$$[illegible]^{B_{..}} + \beta^{B_{..}}\sqrt{2} = 0;$$

$$[illegible]^{B_{..}} a_1\,\mathrm{tg}\,\frac{\theta_1}{2} + a_{10}^{B_{..}} = 0;$$

$$[illegible]^{B_{..}}\,\mathrm{tg}\,\Phi\,\mathrm{tg}^2\frac{\theta}{2}\, a_1 [illegible] + a_{.}^{B_{..}} = 0.$$

For calculat[illegible]on of [illegible]inemat[illegible]ts the following geometrical parameters were used:

S(B-H) = 1.18Å; S([illegible] [illegible] θ = 120°, ∠ H'BH' = θ = 97°

Unharmonia (deviat[illegible]on from harmonicity) was calculated taking into account the "spectroscopic masses" [illegible] hydrogen and deuterium.

Potential function of diborane is characterized by eighty-seven force coefficients which yield thirty-three linearly independent combinations. For determination of these 33 constant values there are available 49 experimentally evaluated frequencies.

Passing to the coordinates of symmetry and again taking into account further additional conditions[1], it is not difficult to obtain symmetrical matrices of kinematic (see Table 1) and force coefficients, multiplying them one obtains secular equations of diborane and its isotope substituents, e.i. $B_2^{11}H_6$, $B_2^{10}H_6$, and $B_2^{10}D_6$. Utilizing ratios of frequencies, as given in (7) the authors of this paper have made calculations of force coefficients of diborane (see Table 2), based on the method of variations.

With this system of force coefficients the numerical values of secular equations, the roots of these equations were calculated by the method of L. G. Magnata [10].

Table 1

Symmetrical Matrices of Kinematic [illegible] of Diborane

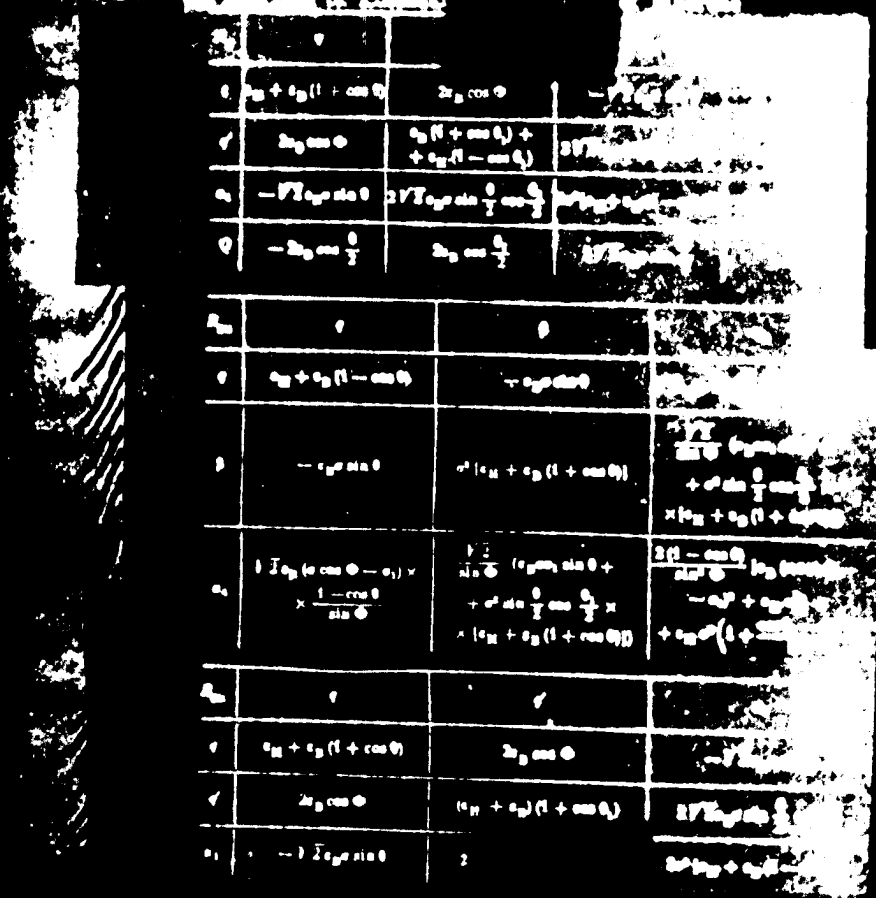


Table 1 (continued)

q	α_1
$\alpha_{11} + \alpha_{12}(1 - \cos\theta)$	$\frac{1 - \cos\theta}{\sin\theta}\alpha_{12}(\alpha\cos\Phi - \alpha_1)$
$\frac{\sqrt{2}(1-\cos\theta)}{\sin\theta}\alpha_{12}(\alpha\cos\Phi - \alpha_1)$	$\alpha_{12}\alpha_1 - \alpha\cos\Phi\alpha_{12} +$ $\alpha_{12}\alpha^2\left(1 + \frac{\cos 2\theta - \cos\theta}{2}\right)$
q'	α_4
$\alpha_{22} + \alpha_{23}(1 - \cos\theta_1)$	$\sqrt{2}\frac{1-\cos\theta_1}{\sin\Phi}[(\alpha_{11} + \alpha_{12})\alpha_1\cos\Phi - \alpha_{12}\alpha$
$\sqrt{2}\frac{1-\cos\theta_1}{\sin\Phi} \times$ $\times[\alpha_{12} + \alpha_{23}\alpha_1\cos\Phi - \alpha_{12}\alpha]$	$\frac{1-\cos\theta_1}{\sin^2\Phi}[2\alpha_{12}(\alpha - \alpha_1\cos\Phi)^2 + \alpha_{12}\alpha^2 +$ $+ 2\alpha_{12}\alpha_1^2\cos^2\Phi)$
q'	α_4
$\alpha_{22}(1 + \cos\theta_1) + \alpha_{23}(1 - \cos\theta_1)$	$-\sqrt{2}\frac{1-\cos\theta_1}{\sin\Phi} \times$ $\times(\alpha_{12}\alpha_1\cos\Phi + \alpha_{12}(\alpha - \alpha_1\cos\Phi)]$
$-\sqrt{2}\frac{1-\cos\theta_1}{\sin\Phi} \times$ $\times[\alpha_{12}\alpha_1\cos\Phi + \alpha_{12}(\alpha - \alpha_1\cos\Phi)]$	$\frac{1-\cos\theta_1}{\sin^2\Phi}\left[\alpha_{12}\alpha^2 + \frac{1}{2}\alpha_{12}\alpha_1^2(1 - \cos\theta_1) \times\right.$ $\left.\times(1 + \cos\Phi) + 2\alpha_{12}(\alpha - \alpha_1\cos\Phi)^2\right]$
$\alpha_1\alpha_2$	$(\alpha_1\alpha_2)\alpha_{12}\alpha^2\frac{1-\cos\theta_1}{\sin^2\Phi}$
B_{23}	$(\alpha_1\alpha_2)\alpha_{12}\alpha^2\frac{1-\cos\theta_1}{\sin^2\Phi} + 2\alpha_{12}\alpha_1^2\frac{1-\cos\Phi}{\sin^2\Phi}$

Designations: $\alpha_1 = \frac{H}{m_1}$ $\alpha = \frac{\alpha(C-H)}{\alpha(B-H)}$ $\alpha_{12} =$
$\theta_1 = \angle H'BH$; $\Phi = \angle HBH'$

TABLE 2

Symmetrical Matrices of Force Coefficients of Diborane*

A_g	q	q'	α_1	α_2
q	6.07	0.09	0.15	0.2
q'	0.09	3.64	-0.2	-0.35
α_1	0.15	-0.2	0.77	-0.38
α_2	0.2	-0.35	-0.38	4

B_{2u}	q	β'	α_4
q	5.92	0	
β'	0	1.02	
α_4	0	-0.025	

B_{1u}	q'	α_4
q'	5.19	0.37
α_4	0.37	0.724

B_{1u}	q	q'	α_1
q	6.12	0.25	0.15
q'	0.25	2.72	-0.2
α_1	0.15	-0.2	0.72

Table 2 (continued)

B_{2g}	q'	q_4	B_{1g}	q	q_4	A_u	q_4	B_{2g}	q_4
q'	2.8	0.19	q	5.7*	0				
q_4	0.19	0.744	q_4	0	0.85	q_4	0.639	q_4	0.31

* in $10^5 cm^{-2}$ units

DISCUSSION OF RESULTS

The results of calculations are shown in Table 3, in which the authors show for each frequency the kind of coordinates. Agreement between the calculated and the observed values of frequency of vibrations is good -- with an average error of 6 cm^{-1} and a maximum error of 28 cm^{-1}. It can, therefore, be concluded that the interpretation of vibrational spectra has been made correctly and the nonplanar ethylene-type model of diborane with two equivalent hydrogen bridges, on the basis of which the frequencies of normal vibrations have been calculated, is considered proven. In favor of the ethylene-type model is also the fact that a small variation of geometrical parameters only slightly affects the values of calculated results obtained. The authors also made two variations in their calculations: 1, using Bell's [8] data $S(B-H) = 1.18Å$; $S_1(B-H') = 1.39Å$, $\angle HBH = 120°$; $\angle H'BH' = 100°$ and 2) $S(B-H) = 1.18Å$; $S_1(B-H') = 1.39Å$; $\angle HBH = \angle H'BH' = 109°28'$. In both cases equally good agreement between the calculated and the observed values of frequencies was obtained. Also the values of force coefficients as calculated in the two variations are only slightly different from the system of force coefficients as shown in Table 2.

The numerical values of force coefficients, as shown in Table 2, corresponding to coordinates of symmetry appear (due to further interdependence between coordinates) as a combination of 67 force coefficients of considerable complexity to be natural coordinates. For this reason the latter cannot be determined, except for those force coefficients which characterize the outer B-H bonds: $K_{g_1}(B-H) = 5.97$; $h_{12} = 0.13$; $h_{13} = 0.03$; $h_{11} = -0.05$ (in $10^5 cm^{-2}$ units). Besides calculation of force coefficients, the calculation of a system of the "influence" coefficients K_{ij}^{-1} of diborane, giving a more complete picture for the molecular force fields [10] was carried out. The calculation of 33 linearly independent coefficients of "influence" was obtained by the usual method of resorting to the inverse matrix values, the remaining coefficients were calculated on the assumption that the "influence" coefficients are subject to the same additional conditions [1] as the vibrational coordinates of symmetry. The calculated data, pertaining to "influence" coefficients are listed in Table 4.

TABLE 3

Interpretation of Vibrational Spectra of Diborane and Its Isotope Substituents (in cm^{-1})

Coordin.	Symm.	$B_2{}^{11}H_6$		$B_2{}^{10}H_6$		$B_2{}^{10}D_6$		$B_2{}^{10}D_2H_4$	$B_2{}^{10}H_4D_2$
		obs.	calc.	obs.	calc.	obs.	calc.	calc.	calc
q(B-H)	A_g	2524	2518		2525	1860	1867	2524	1859
q'(B-H')	A_g	2104	2076		2080	1511	1527	1546	2091
α_1(HBH)	A_g	1180	1181		1189	929	934	1188	951
Q(B-B)	A_g	794	788	820	816	726	701	787	712
α_4(HBH')	A_u	829	829	829	829	592	593	829	593
q'(B-H')	B_{2g}	1747	1744		1747	1273	1279	1298	1752
α_4(HBH')	B_{2g}	1035	1032	1044	1041	870	871	1050	875
q(B-H')	B_{2u}	2612	2609	2625	2626	1999	2003	2626	2006
β(HBH)	B_{2u}	950	955		956	705	696	956	697
α_4(HBH)'	B_{2u}	368	366	368	367	262	269	273	363
q(B-H)	B_{1g}	2591	2582		2601	1980	2000	2601	2000
α_4(HBH')	B_{1g}	920	917	930	930	740	746	930	747
q'(B-H')	B_{1u}	1915	1924	1920	1932	1465	1450	1451	1932
α_4(HBH')	B_{1u}	973	958	977	965	728	731	954	742
α_4(HBH')	B_{3g}	1012	1015		1015	730	726	831	932
q(B-H)	B_{3u}	2525	2526	2528	2531	1845	1852	2531	1852
q'(B-H')	B_{3u}	1602	1607	1606	1612	1205	1194	1199	1607
α_1(HBH)	B_{3u}	1177	1170	1181	1177	881	883	1176	888

The study of "influence" coefficients data allows the following conclusion to be made pertaining to the force fields of diborane: 1) The strength of the outer B-H bonds is twice the strength of the inner B-H' bond. This conclusion is in good agreement with the stretching of the inner B-H' bond (1.33Å) as compared to the outer B-H bond distance (1.18Å). Comparison of "influence" coefficients for the B-H bond in diborane with the B^{11}-H bond in the $B^{11}H_3$ molecule shows increase in bond strength by about 25 percent (the B^{11}-H bond distance is 1.23Å) [11]. 2) The relative weakness of the bond angle HBH' and the large amount of interaction of such types of angles are noted. 3). Comparison of "influence" coefficients K_Q^{-1}(BB) in diborane and in the $B_2{}^{11}H_6$ molecule also shows decrease in the B-B bond in diborane by about 40 percent, in accordance with the increase in the B-B bond distance from 1.59 Å in the $B_2{}^{11}H_6$ molecule to 1.77 Å in the diborane molecule. 4). Also is noted the relative strength of H'BB and BH'B bond angles.

Utilizing the calculated data for the force constants, it was also possible to calculate the vibrational frequencies of deuterium substituted homologues of diborane $H_2B^{10}D_2B^{10}H_2$ and $D_2B^{10}H_2B^{10}D_2$, the vibrational spectra of which have not as yet been interpreted. These predicted values of vibrational frequencies are listed in Table 3.

TABLE 4

Deformation Coefficients of Diborane*

Average Force	Average Force							
	$f(q_1)$	$f(q_5)$	$f(q_7)$	$f(\beta_1)$	$f(q_{12})$	$f(q_{15})$	$f(q_{56})$	$f(q_{5Q})$
$f(q_1)$	0.169	-0.007	-0.004	0.014	-0.028	0.006	-0.004	0.006
$f(q_5)$	-0.003	-0.007	-0.004	0.014	-0.028	0.006	-0.004	0.006
$f(q_6)$	-0.001	0.003	-0.004	0	0	0.001	-0.004	-0.002
$f(q_4)$	0.002	0.003	-0.004	0	0	0.001	-0.004	-0.002
$f(q_5)$	-0.007	0.339	0.017	-0.36	0.071	-0.05	-0.204	-0.069
$f(q_6)$	0.003	-0.031	0.017	0.003	-0.006	-0.063	-0.204	0.273
$f(q_7)$	0.003	-0.016	0.017	0.003	-0.006	-0.036	0.057	-0.015
$f(q_8)$	-0.007	-0.009	0.267	-0.036	0.071	0.043	0.057	-0.022
$f(Q)$	-0.006	0.017	-0.051	-0.051	0.101	0.022	0.267	-0.134
$f(\beta_1)$	0.014	-0.036	-0.051	-0.999	-0.707	0.522	-0.032	0.034
$f(\beta_2)$	0.014	-0.036	-0.051	-0.292	-0.707	-0.118	-0.032	0.034
$f(\beta_3)$	0	0.003	-0.051	-0.153	0.007	-0.165	-0.032	-0.002
$f(\beta_4)$	0	0.003	-0.051	0.147	0.007	0.162	-0.032	-0.002
$f(q_{12})$	-0.028	0.071	0.101	-0.707	1.414	-0.404	0.064	-0.067
$f(q_{34})$	0	-0.006	0.101	0.007	-0.013	0.005	0.064	0.004
$f(q_{15})$	0.006	-0.05	0.022	0.522	-0.404	3.505	0.106	-0.059
$f(q_{16})$	0.006	0.043	0.022	0.522	-0.404	1.594	0.019	-0.046
$f(q_{25})$	0.006	-0.05	0.022	-0.118	-0.404	-2.652	0.106	-0.059
$f(q_{26})$	0.006	0.043	0.022	-0.118	-0.404	-2.163	0.019	-0.046
$f(q_{36})$	0.001	-0.063	0.022	-0.165	0.003	2.186	0.106	-0.047
$f(q_{37})$	0.001	-0.036	0.022	-0.165	0.003	1.746	0.019	0.027
$f(q_{46})$	0.001	-0.063	0.022	0.162	0.003	-2.302	0.106	-0.047
$f(q_{47})$	0.001	-0.036	0.022	0.162	0.003	-1.912	0.019	0.027
$f(q_{58})$	-0.004	-0.204	0.267	-0.032	0.064	0.106	0.587	-0.293
$f(q_{78})$	-0.004	0.057	0.267	-0.032	0.064	0.019	0.238	-0.119
$f(q_{5Q})$	0.006	-0.069	-0.134	0.034	-0.067	-0.059	-0.294	0.305
$f(q_{6Q})$	-0.002	0.273	-0.134	-0.002	0.004	-0.047	-0.294	-0.011
$f(q_{7Q})$	-0.002	-0.015	-0.134	-0.002	0.004	0.027	-0.119	0.057
$f(q_{8Q})$	0.006	-0.022	-0.134	0.034	-0.067	-0.046	-0.119	0.063

CONCLUSIONS

1. Using the method of L. C. Mayants, the frequencies and forms of normal vibrations were calculated for diborane and its isotope substituted homologues. Good agreement was obtained between the calculated and experimental values.

2. The nonplanar ethylene-like diborane model with two equivalent H bridges, on the basis of which the frequencies were calculated, is considered proven.

3. Calculations were also made pertaining to force constants of potential energy of diborane (the force constants and the "influence" coefficients). The peculiarities of the force fields in the diborane molecule were noted.

4. The calculations show errors in the calculations reported in the previous work of Bell [8].

* in 10^{-5} cm^2 units

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